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(54) Title: PROCESS FOR OBTAINING A POLYAMIDE PRODUCT FROM THE SMELT AT A HIGH PRODUCTION RATE		
(57) Abstract <p>The invention relates to a process for obtaining a polyamide product from the smelt, the polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4-butanediamine, as well as to polyamide products obtainable from the smelt, the polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4-butanediamine. Such a process exhibits a high production rate, the polyamide crystallises rapidly and the polyamide has a higher melting point than the polyamides used in a process according to the state of the art. The polyamide objects have mechanical properties that are comparable with those of polyamide products with which the polyamide consists essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,6-hexanediamine. Preferably 1,10-decanedioic acid or 1,12-dodecanedioic acid is chosen as the dicarboxylic acid. The invention also relates to a process for the preparation of a polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4-butanediamine in which, successively, a first polymerisation of the diacid with 8-14 C-atoms and 1,4-butanediamine is effected in the fluid phase, resulting in a low-molecular polymer, followed by a post-polymerisation of the low-molecular polymer thus obtained in the solid phase, and to a polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4-butanediamine, the number average molar mass being at least 15,000 g/m.</p>		

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PROCESS FOR OBTAINING A POLYAMIDE PRODUCT FROM THE
SMELT AT A HIGH PRODUCTION RATE

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The invention relates to a process for obtaining a polyamide product from the smelt, the polyamide consisting essentially of units derived from
10 an aliphatic dicarboxylic acid with 8-14 C-atoms and an aliphatic diamine.

In the context of this application, 'essentially' is understood to be at least 50 % by weight, preferably at least 75 % by weight, more
15 preferably at least 85 % by weight, most preferably at least 90 % by weight.

In the context of this application, a 'product' is understood to be an object extending in 1, 2 or 3 dimensions, for example a fibre, a monofilament, a foil, a film, a plate or a moulded part. As a fibre, such a polyamide product can be used in applications demanding a high wear resistance, for example in
20 carpets, textile fibres or technical yarns. A well-known monofilament application is for example the application as fishing yarn or as toothbrush bristles. As a foil, such a polyamide product can be used for example as packaging material for foodstuffs, for example sausage or cheese. As a moulded part, such a
25 polyamide product can be used for example in the automotive industry, in particular to replace metal parts, in order to lower a car's weight, or for applications 'under the bonnet'. A polyamide moulded part can also often be used in the E&E industry, for
30 example as housing for electric or electronic components and for components of surface-mounted devices.

35

A prerequisite for the aforementioned polyamide products is that said products have excellent mechanical properties, in particular a high degree of stiffness, in particular a high degree of stiffness in
5 a conditioned state, a high degree of toughness and a high impact resistance and little creep. The polyamide product must have a high heat distortion temperature, it must be chemically resistant to all kinds of chemicals, such as de-icing salt, oil and grease, and
10 it must absorb little moisture, so that a good dimensional stability can be obtained.

The polyamides that are used most often for such a polyamide product are polyamides with which 1,6-diaminohexane is chosen as the aliphatic diamine, more
15 in particular the polyamides with which 1,6-diaminohexane is chosen as the aliphatic diamine and 1,10-decanedioic acid (Nylon 6,10) or 1,12 dodecanedioic acid (Nylon 6,12) as the dicarboxylic acid with 8-14 C-atoms.

20 Such a polyamide product can be prepared using a process in which a melt of the polyamide is cooled in a particular shape. Fibres and monofilaments can be prepared for example via the melt-spinning method; foils can be prepared via the extrusion method
25 and moulded parts can be prepared for example using the injection-moulding method. One of the features that said methods for the preparation of polyamide products from the smelt have in common is that the method's production rate, for example the number of products
30 that can be made per unit of time or for example the length of the spun fibre or extruded foil per unit of time, cannot be increased limitlessly with the current technical means and seems to have reached the limit inherent to the polyamide employed. In particular this

relates to a process for preparing a thick moulded part, i.e. a moulded part with a wall thickness of more than 2 mm, and a process for preparing a fibre that is spun at a speed of more than 5,000 m/min (the so-called
5 high-speed spinning fibre).

The process according to the state of the art presents the disadvantage that the production rate of the process in which a melt of the polyamide is cooled in a particular shape is relatively slow. A low
10 production rate is not desirable and there is hence a need to prepare the product at a higher production rate.

The inventors have now found that the production rate is to a great extent dependent on the
15 crystallisation rate of the polyamide used to prepare the polyamide product. A conventional means that is used to raise the crystallisation rate of polymers in general is adding heterogeneous additives to the melt, for example talk and metal salts, for example sodium
20 benzoate. This however presents the disadvantage that an extra processing step will in many cases be required.

The aim of the invention is to provide a process for obtaining a polyamide product from a smelt, the polyamide consisting essentially of units derived
25 from an aliphatic dicarboxylic acid with 8-14 C-atoms and an aliphatic diamine, the process having an improved production rate.

This aim was achieved by choosing 1,4-butanediamine as the aliphatic diamine.

30 Surprisingly, it was found that the crystallisation rate of the polyamide product was increased by choosing 1,4-butanediamine as the aliphatic diamine in the process according to the invention, as a result of which the polyamide product

could be prepared at a high production rate.

Another advantage of the polyamide process according to the invention is the higher melting temperature of the polyamide product, in comparison
5 with a polyamide product with which the polyamide consists essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,6-hexanediamine, as a result of which the polyamide product according to the invention can be used in high-
10 temperature applications.

The product according to the invention also shows comparable mechanical properties, a comparable wear resistance in a conditioned state and a comparable absorption of moisture, in comparison with a polyamide
15 product with which the polyamide consists essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,6-hexanediamine, so that the product according to the invention is in principle suitable for the same applications.

20 A product is known from DE-A-1669657 which consists of 95 % by weight polypropylene and 5 % by weight of a polyamide prepared from 1,4-butanediamine and decamethylene dicarboxylic acid. Such a product shows a greater elongation, in comparison with a
25 product that consists exclusively of polypropylene.

As the aliphatic dicarboxylic acid with 8-14 C-atoms is chosen a dicarboxylic acid from the group comprising 1,8-octanedioic acid, 1,9-nonanedioic acid, 1,10-decanedioic acid, 1,11-undecanedioic acid, 1,12-dodecanedioic acid, 1,13-tridecanedioic acid and 1,14-tetradecanedioic acid. Preferably, 1,10-decanedioic
30 acid and 1,12-dodecanedioic acid is chosen.

The polyamide product may also contain other polymers, or conventional additives, for example

flame retardants, nucleating agents, fillers, for example glass fibres, pigments and processing aids.

The process is suitable for obtaining polyamide products in all applications in which the
5 polyamide products according to the state of the art are used, for example as a fibre, monofilament, foil, film, plate or moulded part.

The polyamide products obtained by the process according to the invention may also contain
10 other polymers. Then, the product contains 6 - 100 % by weight of the polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4, preferably 50 - 100 % by weight, more preferably 60 - 100 % by weight, most preferably 70 -
15 100 % by weight.

The product can also be used in all current applications according to the state of the art in which polyamide products are used that consist essentially of units derived from caprolactam (Nylon 6) or of units
20 derived from 1,6-hexanedioic acid and 1,6-hexanediamine (Nylon 6,6).

In particular, the product is used as a thick moulded part with a wall thickness of more than 2 mm and as a fibre, in particular as a high-speed-
25 spinning fibre.

The product is obtained from the smelt by any process in which a product is formed from a smelt, for example by casting, moulding, extrusion, spinning or any equivalent process, known to a skilled person.

30 The invention also relates to a process for the preparation of a polyamide consisting essentially of units derived from a dicarboxylic acid with 8-14 C-atoms and 1,4-butanediamine.

Such a process is known from Dreyfuss,

Journal of Polymer Science, Vol 11(2), 201-216 (1973),
in which is described a process in which the
polymerisation is carried out in a mixture of two non-
miscible solvents (water and perchloroethylene) with
5 the aid of the dicarboxylic acid chloride of 1,12-
dodecanedioic acid and 1,4-butanediamine.

The disadvantage of said method is that it
does not result in a high yield, it does not yield a
polymer with a number average molar mass of more than
10 15,000, it is very corrosive and it is hence neither
environmentally nor commercially attractive for use on
a large scale.

The inventors have now found that a
polyamide consisting essentially of units derived from
15 a dicarboxylic acid with 8-14 C-atoms and 1,4-
butanediamine can be prepared by successively carrying
out a first polymerisation of the dicarboxylic acid
with 8-14 C-atoms and 1,4-butanediamine in the fluid
phase, resulting in a low-molecular polymer ($M_n = 1,000$
20 - 4,000 g/mol), followed by an post-polymerisation of
the low-molecular polymer thus obtained in the solid
phase until a polymer with the desired molar weight is
obtained.

In particular, a polyamide is prepared
25 which consists essentially of units derived from a
dicarboxylic acid with 8-14 C-atoms and 1,4-
butanediamine having a number average molar mass of at
least 15,000 g/mol. A product prepared with such a
polyamide from the smelt presents the advantage that it
30 can be prepared at an elevated production rate.

In a preferred embodiment a prepolymer is
prepared in an aqueous mixture of about 85-90 % by
weight salt of the dicarboxylic acid and the diamine,
at a temperature of 180-240°C and at a pressure of 10-

15x10⁵ Pa. The aftercondensation of this prepolymer subsequently takes place while a N₂/water vapour mixture is passed over it, at a temperature that lies about 10-50°C below the polymer's melting point, for as long as
5 it takes to obtain the desired molar mass (M_n is typically 15,000-30,000 g/mol).

The invention will now be further elucidated with reference to the following examples, without being limited thereto.

10

Examples

Example I : Preparation of Nylon 4,10

a. Prepolymerisation

15 350 grams of 1,10-decanedioic acid (Acros Organics), 235 grams of 1,4-butanediamine solution (67 % by weight in water) (DSM N.V.) and 338 grams of water are stirred in a 1.4-litre autoclave for 30 minutes at 90°C such that a 55 % by weight salt solution is
20 obtained. Then water is removed through distillation by first raising the temperature in 10 minutes to 180°C, removing half of the amount of water through distillation and then raising the temperature to 200°C and removing an amount of water through distillation
25 such as to obtain a 90 % by weight aqueous salt solution. Then the reactor is completely closed, the distillation is stopped and the temperature is raised to 227°C and the prepolymerisation begins. The water present and the high temperature cause the pressure to
30 rise slowly. The pressure at the end of the prepolymerisation is about 12x10⁵ Pa. The prepolymerisation is performed during 1/2 hour at a constant temperature, after which the content of the autoclave is flashed in a nitrogen atmosphere. The

prepolymer is cooled in a nitrogen atmosphere.

b. Postcondensation

The prepolymer granules obtained according
5 to step a) are sieved so that the fraction having a
diameter of between 1 and 2 mm is obtained. This
fraction is introduced into either a static bed
(capacity approximately 50 g of solid substance) or a
tumble dryer (capacity approximately 10 litres) and
10 postcondensed at an elevated temperature (about 25°C
below the polymer's melting point) in a nitrogen/water
vapour (75/25 % by volume) atmosphere for 24 hours.
Then the polymer granules were cooled to room
temperature. From the polymer thus prepared a number of
15 rods and plates were injection-moulded.

Example II : Preparation of Nylon 4,12

In the same way as in Example I, an
analogous amount of Nylon 4,12 was prepared, using as
20 starting materials 1,4 -butanediamine (DSM N.V.) and
1,12-dodecanedioic acid (Acros Organics) in the same
molar ratio. From the polymer thus prepared a number of
rods and plates were injection-moulded.

25 Example III : Preparation of Nylon 4,8

In the same way as in Example I, an
analogous amount of Nylon 4,8 was prepared, using as
starting materials 1,4 -butanediamine (DSM N.V.) and
1,8-octanedioic acid (Acros Organics) in the same molar
30 ratio. From the polymer thus prepared a number of rods
and plates were injection-moulded.

Comparative Example A : Preparation of Nylon 6,10.

In the same way as in Example I, an amount of Nylon 6,10 was prepared, using as starting materials 1,6-hexanediamine (Acros Organics) and 1,10-decanedioic acid (Acros Organics) in the same molar ratio. From the polymer thus prepared a number of rods and plates were injection-moulded.

Nylon 6,10 is also commercially available from for example the company Nyltech (France).

10

Comparative Example B : Preparation of Nylon 6,12.

In the same way as in Example 1, an amount of Nylon 6,12 was prepared, using as starting materials 1,6-hexanediamine (Acros Organics) and 1,12-dodecanedioic acid (Acros Organics) in the same molar ratio. From the polymer thus prepared a number of rods and plates were injection-moulded.

Nylon 6,12 is also commercially available from for example the company DuPont (USA).

20

Molecular characterisation of the polyamides of Examples I-III and Comparative Examples A-B.

The molecular characteristics of the polyamides of Examples I-III and Comparative Examples A-B were determined as follows.

The viscosity number was determined in formic acid ($c = 0.005$ g/ml) at 25°C with the aid of an Ubbelohde (Schott type 530-10/1).

The relative viscosity was determined in H₂SO₄ at 25°C with the aid of an Ubbelohde (Schott type 530-10/1).

The carboxyl end groups were potentiometrically determined in o-cresol by means of a titration with tetrabutyl ammonium hydroxide.

The amino end groups were potentiometrically determined in phenol by means of a titration with hydrochloric acid.

The total concentration of pyrrolidine end groups of the polyamides based on 1,4-butanediamine was determined with a through-flow fluorimeter via detection of a fluorescent compound formed in a reaction of pyrrolidine with NBD-chloride (4-chloro-7-nitrobenzo-2-oxa-1,3-diazole). The molecular characteristics of the polyamides are summarised in Table 1. From Table 1 it is evident that all the polyamides in Table 1 have approximately comparable molar masses.

Table 1: Molecular characterisation of the polyamides of Examples I-III and Comparative Examples A-B.

Property	Unit	Example I	Example II	Example III	Comparative Example A	Comparative Example B
Polyamide		Nylon 4,10	Nylon 4,12	Nylon 4,8	Nylon 6,10	Nylon 6,12
Molar mass (M_n)	Grams/ mole	17,200	19,200	26,000	18,900	16,400
Viscosity number	ml/gram	-	-	206	-	-
Relative viscosity		3.40	2.58	3.61	2.99	2.35
Concentration of amine end groups	meq/gram	0.020	0.047	0.014	0.021	0.036
Concentration of carboxylic acid end groups	meq/gram	0.058	0.026	0.054	0.085	0.086
Concentration of pyrrolidine end groups	meq/gram	0.038	0.031	0.009	0	0

Determination of the crystallisation properties

The thermal characterisation of the polyamides was carried out using a Perkin Elmer DSC-7. The measurements were carried out in an N₂ atmosphere at
5 a block temperature of the DSC apparatus of -10°C.

Dynamic measurements

The melting (T_m) and crystallisation temperature (T_c) were determined by means of dynamic
10 measurements using a heating and cooling rate of 20°C/min. A polyamide was successively heated to above its melting temperature, cooled to below the crystallisation temperature and heated a second time. The difference between the melting temperature inferred
15 from the second heating curve and the crystallisation temperature, the subcooling ($T_{m2} - T_c = \Delta T$), is a measure of a polyamide's crystallisation rate. The results are summarised in Table 2. From Table 2 it is evident that less subcooling is required to effect the
20 crystallisation of Nylon 4,10 and Nylon 4,12 in comparison with Nylon 6,10 and Nylon 6,12, respectively. By way of comparison: the degree of subcooling required for Nylon 6 at a cooling rate of 20°C/min is 47°C, while it is 43°C for Nylon 6,6. It
25 will be clear that with the process according to the invention less subcooling is needed and hence faster crystallisation results.

Table 2: Dynamic crystallisation of the polyamides of Examples I-III and Comparative Examples A-B.

Property	Unit	Example I	Example II	Example III	Comparative Example A	Comparative Example B
Polyamide		Nylon 4,10	Nylon 4,12	Nylon 4,8	Nylon 6,10	Nylon 6,12
T_m	°C	249	237	261	225	217
T_m	°C	249	238	262	223	215
T_c	°C	210	205	222	179	181
$T_m - T_c$ (ΔT)	°C	39	33	40	44	34

Kinetic measurements

The half-life period for crystallisation ($t_{1/2}$), which is the amount of time required to realise half of the total degree of crystallisation realisable, was determined via isothermal crystallisation. A sample of polyamide was heated in an N_2 -atmosphere to approximately 40°C above its melting point. The polyamide was kept at this temperature for half an hour, to enable all the remains of the crystalline phase to disappear, after which the temperature was quickly returned to a temperature between the glass transition temperature and the melting temperature. The sample was kept at this temperature, the crystallisation temperature, for an hour, to enable it to crystallise, while the flow of heat was measured with a DSC. This experiment was repeated four times at four different crystallisation temperatures. The half-life period for crystallisation ($t_{1/2}$) was calculated from the measurements thus obtained. This parameter characterises the polymer's ability to crystallise. A lower value implies a greater ability to crystallise. The results are summarised in Table 3. From Table 3 it is evident that Nylon 4,10 and Nylon 4,12 crystallise faster at comparable subcooling values than Nylon 6,10 and Nylon 6,12, respectively.

Table 3: Kinetic crystallisation of the polyamides of Examples I-III and Comparative Examples A-B.

Example I				Comparative Example A				Example II				Comparative Example B				Example III			
Nylon 4,10				Nylon 6,10				Nylon 4,12				Nylon 6,12				Nylon 4,8			
T (°C)	ΔT (°C)	T _{1/2} (min)	T (°C)	ΔT (°C)	T _{1/2} (min)	T (°C)	ΔT (°C)	T (°C)	ΔT (°C)	T _{1/2} (min)	T (°C)	ΔT (°C)	T _{1/2} (min)	T (°C)	ΔT (°C)	T (°C)	ΔT (°C)	T _{1/2} (min)	T (°C)
230	19	2.2	202	21	3.0	223	15	223	15	1.8	194	21	4.4	241	21	241	21	3.2	241
233	16	3.6	205	18	6.1	225	13	225	13	3.2	198	17	7.3	243	19	243	19	6.6	243
237	12	7.9	208	15	10.5	227	11	227	11	7.1	200	15	9.9	245	17	245	17	8.5	245
240	9	19	210	13	18.5	229	9	229	9	11.2	202	13	14.7	247	15	247	15	10.4	247

Determination of the mechanical properties

To determine the mechanical properties of the polymer products, the polymer was first dried at 105°C in an N₂-atmosphere at reduced pressure for 16
5 hours. Specimens for tensile and IZOD testing were injection-moulded using an Arburg 5, at an injection-moulding temperature of between 245 and 290°C. The mould temperature was 80°C.

The mechanical properties were determined
10 using dry or conditioned (conditioning conditions: 50% relative humidity at 23°C to equilibrium) tensile test specimens. The results are summarised in Table 4. By way of comparison (Comparative Example C), the properties of Nylon 6, determined using the commercial
15 grade Akulon 123 (DSM N.V., the Netherlands) are also indicated. From Table 4 it is evident that the polyamide tensile test specimens according to the invention show mechanical properties that are at least comparable with those according to the state of the
20 art.

Table 4: Mechanical properties of the polyamides of Examples I-III and Comparative Examples A-B.

n.d. = not determined.

Property	Unit	Standard	Ex. I	Ex. II	Comp. Ex. A	Comp. Ex. B	Comp. Ex. C
Polyamide			Nylon 4,10	Nylon 4,12	Nylon 6,10	Nylon 6,12	Nylon 6
Dry							
Modulus of elasticity	MPa	ISO 527/1A	3,180	2,790	2,450	2,570	3,000
Tensile strength	MPa	ISO 527/1A	77	49	48	62	78
Elongation at break	%	ISO 527/1A	9.8	36	29	4	80
IZOD, notched	kJ/mm ²	ISO 179/1eA	3.2	5.4	5.5	5.4	5.5
IZOD, unnotched	kJ/mm ²	ISO 179/1eU	45	186	188	43	n.d.
Conditioned							
Modulus of elasticity	MPa	ISO 527/1A	1,680	n.d.	n.d.	n.d.	800
Tensile strength	MPa	ISO 527/1A	56	n.d.	n.d.	n.d.	41
Elongation at break	%	ISO 527/1A	114	n.d.	n.d.	n.d.	> 300
IZOD, notched	kJ/mm ²	ISO 179/1eA	6.9	n.d.	n.d.	n.d.	36

Determination of the resistance to stress cracking

The resistance to stress cracking of polyamide products was determined by subjecting a polyamide compressed plate with a thickness of 1 mm to
5 a pressure of 3 N/mm² at 75°C, while the compressed plate was submerged in an aqueous ZnCl₂ solution (50 % by weight). The amount of time required for the plate to crack (cracking time) is measured.

Before the test, the polyamide compressed
10 plate was first dried for 24 hours in a vacuum at 90°C. The test showed that a compressed plate of Nylon 4,12 showed a resistance to stress cracking that is at least the same as a that of a compressed plate of Nylon 6,12. By way of comparison: the cracking time of a compressed
15 plate of Nylon 6 was substantially lower than that of both Nylon 4,12 and Nylon 6,12.

C L A I M S

1. Process for obtaining a polyamide product from the
5 smelt, the polyamide consisting essentially of
units derived from an aliphatic dicarboxylic acid
with 8-14 C-atoms and an aliphatic diamine,
characterised in that the diamine is 1,4-
butanediamine.
- 10 2. Process according to Claim 1, characterised in
that the polyamide product consists of 6 - 100 %
by weight of polyamide.
3. Process according to Claim 1, characterised in
that the polyamide product consists of 50 - 100 %
15 by weight of polyamide.
4. Process according to Claim 1, characterised in
that the polyamide product consists of 70 - 100 %
by weight of polyamide.
5. Process according to any one of Claims 1-4,
20 characterised in that as the aliphatic
dicarboxylic acid with 8-14 C-atoms is chosen a
dicarboxylic acid from the group comprising 1,8-
octanedioic acid, 1,9-nonanedioic acid, 1,10-
decanedioic acid, 1,11-undecanedioic acid, 1,12-
25 dodecanedioic acid, 1,13-tridecanedioic acid and
1,14-tetradecanedioic acid.
6. Process according to Claim 5, characterised in
that as the aliphatic dicarboxylic acid with 8-14
C-atoms is chosen 1,10-decanedioic acid or 1,12-
30 dodecanedioic acid.
7. Process according to any one of Claims 1-6,
characterised in that the product obtained is a
fibre, monofilament, foil, film, plate or moulded
part.

8. Process according to any one of Claims 1-7, characterised in that the process comprises a step in which the product is obtained by cooling a polyamide melt.
- 5 9. Polyamide product, obtainable from the smelt, the polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4-butanediamine.
- 10 10. Process for the preparation of a polyamide that consists essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4 butanediamine, characterised in that, successively, a first polymerisation of the dicarboxylic acid with 8-14 C-atoms and 1,4-
15 butanediamine is effected in the fluid phase, resulting in a low-molecular polymer, followed by an post-polymerisation of the low-molecular polymer thus obtained in the solid phase.
- 20 11. Process according to Claim 10, characterised in that a polyamide with a number average molar mass of at least 15,000 g/mol is prepared.
- 25 12. Polyamide consisting essentially of units derived from an aliphatic dicarboxylic acid with 8-14 C-atoms and 1,4 butanediamine, characterised in that the number average molar mass is at least 15,000 g/mol.
- 30 13. Processes for obtaining a polyamide product and polyamide products as described and elucidated in the examples.

INTERNATIONAL SEARCH REPORT

National Application No.

PCT/NL 99/00505

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G69/26 C08G69/28 C08G69/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 459 714 A (WOLFES WOLFGANG ET AL) 5 August 1969 (1969-08-05) examples 5,6 column 3, line 58-64 ---	1-6,9,10
A	DE 16 69 657 A (BASF AG) 6 May 1971 (1971-05-06) cited in the application example 2D page 3, line 4-21 ---	1
A	JOURNAL OF POLYMER SCIENCE. POLYMER PHYSIC EDITION, vol. 11, no. 2, 1973, pages 201-216, XP002099708 cited in the application page 203, paragraph 3 -page 205, paragraph 4 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 October 1999

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20/10/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00505

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